

PORTLAND HARBOR RI/FS
REMEDIAL INVESTIGATION REPORT

APPENDIX D4.4
**PATTERNS AND TRENDS OF DDx, PAHs, and TPH IN
TRANSITION ZONE WATER**

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APPENDIX D4.4 PATTERNS AND TRENDS OF DDX, PAHS, AND TPH IN TRANSITION ZONE WATER

D4.4.1 Introduction

Section 5.5 of the remedial investigation (RI) report discusses the extent of concentrations of indicator contaminants in transition zone water (TZW). This appendix provides additional details on the nature of three grouped contaminants, DDX¹, polycyclic aromatic hydrocarbons (PAHs), and total petroleum hydrocarbons (TPH) analyzed in TZW, by examining the patterns in the constituent contaminants that make up these compound groups. As mentioned in Section 5.5, polychlorinated biphenyls were not analyzed in TZW, and only two TZW sampling locations were analyzed for polychlorinated dibenzo-p-dioxins/furans; these chemicals are not included in this TZW nature and extent discussion. The detail provided here helps inform discussion of the conceptual site model (Section 10) and identification of potential sources and contaminant transport.

Stacked bar charts, designed to reveal potential distinctive patterns in the relative abundance of grouped chemical components (e.g., homologs, isomers), are one tool used to examine the nature of contaminants in this appendix.² Stacked bar charts of total DDX, total PAHs, and TPH present, for each individual TZW sample, the fractional contribution of each individual constituent of the total concentration (detected sums only). The total sum concentration is also denoted on the figure with a black line (scale on the right-hand y-axis). Station location labels are provided on the x-axis, along with discharge conditions. Samples are organized along the x-axis according to descending river mile order, grouped by understanding of groundwater discharge areas as discussed in detail in Appendix C2 of the RI report. Where available, peeper (“PR”), filtered and unfiltered Trident (“TR”), and Geoprobe (“GP”) data are shown for each sample location. Sample IDs for filtered results (“-f” in the sample ID) are indicated by highlighting. Deeper Trident samples are denoted by “-90”, “-120”, or “-150” in the sample ID, referring to depth below mudline (bml) in centimeters. Further, field duplicate samples on these figures are denoted by “dup” in the sample ID.

Also note that the TZW data set was generated for the purposes of assessing TZW offshore of upland groundwater plumes with likely or known complete pathways to the river; therefore, the data set does not cover all areas where TZW may be affected by unknown plumes or TZW quality impacted by contaminated sediments. Specifically,

¹ DDX represents the sum of the 2,4'- and 4,4'- isomers of dichloro-diphenyl-dichloroethane (DDD), dichloro-diphenyl-dichloroethene (DDE), and dichloro-diphenyl-trichloroethane (DDT).

² It is important to note that patterns apparent in the stacked bar charts should be interpreted with caution. Changes in chemical composition and apparent trends shown by the bar charts may be indicative of significant patterns (e.g., distinctive source contributions), or they may be within the range of normal data variability. Source identification and allocation are complex multivariate problems. The pattern shifts discussed here based on stacked bar chart presentations may be suggestive, but cannot be interpreted directly as or attributed to localized sources. Such a characterization would require rigorous quantitative forensic analysis, which is outside the scope of this RI/FS.

the data set is focused on the offshore area of nine sites, identified as high-priority, Category A upland groundwater sites due to a confirmed or reasonable likelihood for discharge of upland groundwater contaminants of interest to Portland Harbor. Consideration of pore water chemistry affected by in-river sediment contamination is evaluated in Section 6 of the RI report through equilibrium partitioning calculations based on the large data set of sediment concentrations.

Groundwater seep data are limited and do not allow for definitive conclusions, so are not evaluated here. Only one seep, Outfall 22B (at the Rhone Poulenc site), is relevant for use in the baseline human health risk assessment. At this location, groundwater infiltrates into the outfall pipe, which subsequently discharges to a beach. The beach where Outfall 22B discharges was identified as a potential transient use area, so exposure to the groundwater seep in that beach by transients is considered a potentially complete pathway. For most analytes evaluated, Outfall 22B concentrations were near or below detection limits and were well below nearby upland groundwater and TZW concentrations.

D4.4.2 Patterns and Trends of DDx in TZW

DDx was measured in TZW at ten locations offshore of the former Acid Plant area of the Arkema site, as well as at one location offshore of the adjacent Rhone Poulenc site. Patterns and trends of DDx distribution are evaluated based on maps presented in Section 5.5.1 and stacked bar charts presented in this appendix. Evaluation of these patterns and trends for DDx is limited due to low sample size and detection frequencies; however, development of basic conclusions regarding chemical composition and the influence of filtration and sample depth is possible, as presented in the following paragraphs.

As shown on the histograms on Map 5.5-1, the observed ranges of DDx concentrations are generally higher in unfiltered samples as compared to the observed range for filtered and peeper samples. This tendency observed in the histogram ranges is upheld in a point-by-point assessment of the seven collocated filtered and unfiltered Trident pairs, where unfiltered sample concentrations are over 90 percent greater than filtered samples in four pairs collected offshore of the Arkema Acid Plant area. Higher sample concentrations in unfiltered samples as compared to filtered samples is expected for these highly hydrophobic chemicals, indicating the presence of DDx sorbed to solids larger than the filter diameter ($>0.45\ \mu\text{m}$) in the unfiltered Trident samples. These results indicate that the unfiltered samples in the former Acid Plant area are likely affected by intake of sediment in the unfiltered sampling process. Further, the highest filtered sample result is observed offshore of the Rhone Poulenc site, whereas the collocated unfiltered result offshore of the Rhone Poulenc site ($0.21\ \mu\text{g/L}$) is well below the average ($1.78\ \mu\text{g/L}$) of all measured unfiltered concentrations; this result suggests that uptake of solids did not influence the unfiltered concentrations measured at RP-03-C.

Comparison of total DDx concentrations in unfiltered samples at the three sample locations (RP-03-C, AP-03-A, R2-AP-02) where both shallow (0 to 38 cm bml) and deep (90 to 150 cm bml) TZW samples were collected shows that the deeper samples consistently have higher concentrations than the shallow samples at AP-03-A and R2-AP-02. However, at RP-03-C, the deeper sample is generally comparable to the corresponding shallow samples in both filtered and unfiltered data sets.

Figure D4.4-1 presents bar charts showing percent composition of the six DDx congeners in the 15 samples with a detected total DDx result. The chart only presents samples where all six DDx congeners were analyzed.³ Samples are organized along the x-axis in groups referring to groundwater discharge zones. (These zones are indicative of areas of similar groundwater discharge conditions, as described in Appendix C2.) On these figures, sample IDs indicate sample location, sample method, sample depth, and field duplicates, as described above. Evaluation of the stacked bar chart in Figure D4.4-1 yields the following observations:

- The two duplicate sample pairs (AP-03-A-TR-f and AP-03-A-TR-f-dup; AP-03-A-TR-uf and AP-03-A-TR-uf-dup) show good reproducibility in composition trending.
- Two of the shallow and deep sample pairs show similar compositions at both depths. The shallow and deep pair collected at R2-AP-02-TR-uf has an extreme concentration difference and shows different composition between the shallow and deep result.
- The bar chart trends further support the overall observed trends noted above in discussions of spatial distribution and filtration effects. The highest total DDx concentrations (concentration indicated by the black line corresponding to the right y-axis) are mainly associated with unfiltered samples (filtered sample IDs are highlighted). These total concentration peaks (designated by the black line) correspond to DDx compositions dominated by 4,4'-DDT plus 4,4'-DDD.

In summary, for the limited data set available, the highest DDx concentrations were observed in unfiltered deep (90 to 150 cm bml) samples collected offshore of the former Acid Plant area. Filtration greatly reduced DDx concentrations measured offshore of the Acid Plant, indicating that DDx is present on solids. The highest filtered sample result is observed offshore of the Rhone Poulenc site. Filtration did not significantly reduce DDx concentrations measured at the single Rhone Poulenc sample location, and the unfiltered results offshore of the Rhone Poulenc site are below the average of unfiltered concentrations observed offshore of the former Acid Plant site. Further, offshore of the former Acid Plant area, TZW concentrations are generally greater at depth (90 to 150 cm bml) as compared those in shallow TZW (0 to 38 cm bml). Conclusions about completeness of the groundwater pathway are presented in detail

³ The 2004 Pilot Study samples were analyzed for 4,4'-DDx congeners only, and are therefore not shown on the stacked bar chart in Figure D4.4-1.

with additional lines of evidence in Appendix C2 and summarized in Section 4 of the RI report.

D4.4.3 Patterns and Trends of PAHs in TZW

PAHs were sampled at six of the TZW sites (Kinder Morgan, ARCO, ExxonMobil, Gasco, Siltronic, and Willbridge Terminal). As shown on the river-mile-specific portions of the histograms of Maps 5.5-2a–e and described above, the observed ranges of unfiltered total PAH concentrations for each river mile sampled are higher than filtered and peeper-sampled concentrations. This trend is upheld in a point-by-point assessment of the 34 collocated filtered and unfiltered Trident pairs for total PAHs. Looking at the filtered and unfiltered Trident pairs, filtration decreased the average total PAH concentration by 24 percent, with a maximum decrease of up to 99 percent (AR-02-B). Note that the apparent large decrease in the total PAHs concentration range with filtration seen on the harbor-wide portion of the histograms is largely attributable to the lack of filtered PAH samples from the non-LWG investigations offshore of the Siltronic and Gasco sites. The Siltronic and Gasco unfiltered results account for most of the >1,000 µg/L values.

By examining the effects of filtration, the effects of individual PAH hydrophobicity can be seen in the data set. As shown on inset histograms on Maps D4.2-2a–d and D4.2-4a–d, the large, hydrophobic carcinogenic polycyclic aromatic hydrocarbons (cPAHs) and benzo(a)pyrene (BaP) show extreme differences between filtered and unfiltered results (with an average of over 95 percent decrease in a paired sample comparison for both cPAHs and BaP), suggesting that these chemicals are present on solids >0.45 µm in diameter in unfiltered TZW samples. In contrast, the smaller, less hydrophobic individual PAHs have a lesser tendency to bind to sediment and would be expected to be less affected by filtration, contributing the lower net effect of filtration on total PAHs concentrations. This filtration effect on total PAHs is therefore a function of the composition of each sample.

Comparison of total PAHs concentrations in the seven collocated deep and shallow (0 to 38 cm bml) TZW samples shows that the unfiltered deep samples consistently exhibit higher concentrations than the corresponding shallow samples. In some cases, the unfiltered, deep sample concentrations are up to 2 orders of magnitude greater than the collocated shallow samples. The three filtered deep/shallow sample pair results, however, show no clear relative trend. As with total PAHs, analysis of collocated deep/shallow sample pair results shows that unfiltered concentrations of high-molecular-weight polycyclic aromatic hydrocarbons (HPAHs), cPAHs, and BaP are generally much higher in deep samples. For naphthalene, 17 collocated deep (90 to 150 cm bml) and shallow (0 to 38 cm bml) Trident samples and 24 collocated deep (91 cm bml) and shallow (31 cm bml) Geoprobe samples were collected. In general, for the high (>1,000 µg/L) concentration samples collected from RM 6 to 7, shallow samples showed somewhat higher concentrations than collocated deep samples. For other parts of the Study Area, no clear trends with depth were observed for naphthalene.

Stacked bar charts showing percent composition of detected total PAHs sums are shown on Figures D4.4-2a–f. The charts present total PAHs concentration (indicated by the black line corresponding to the right y-axis), as well as the fraction of the total contributed by each of the 17 PAHs. Charts are presented for each relevant TZW study site, with samples organized along the x-axis in groups referring to groundwater discharge zones. These zones are indicative of areas of similarly mapped groundwater discharge conditions offshore of the given study site and are presented and discussed in detail in Appendix C2.

There are a several patterns apparent in these stacked bar charts. First, duplicate sample pairs show good reproducibility in composition trending. Second, the shallow and deep pairs frequently show variable compositions, particularly in cases where the deeper concentration is greater than the shallow concentration (e.g., EM04C-TR-uf-150, which has an extreme concentration difference between the shallow and deep result). This may reflect weathering in the biologically active zone and/or differences in PAH composition in sediment with depth. Next, a distinct chemical composition is generally present at sample locations with very high total PAHs concentrations. Acenaphthene is the dominant component of total PAHs sums in most samples; however, at sample locations with total PAHs greater than $\sim 1,000 \mu\text{g/L}$, naphthalene concentrations clearly dominate the composition. This result is interesting to evaluation of TZW because naphthalene is the most mobile chemical of the PAHs. This composition pattern is apparent in the bar charts for TZW data offshore of the Gasco and Siltronic sites (Figures D4.4-2d–e). These areas correspond to suspected discharge zones offshore of the Siltronic and Gasco sites (discussed in detail in Appendix C2). Composition trends with concentration and location are less apparent at the other TZW study sites, where total PAHs concentrations cover a much lower concentration range.

In summary, of the sites sampled, total PAHs concentrations were found to be highest offshore of the Gasco and Siltronic sites. Total HPAHs, total cPAHs, and BaP results showed similar distribution and filtration patterns. Because low-molecular-weight polycyclic aromatic hydrocarbons (LPAHs) tend to compose the majority of the total PAHs concentrations, LPAH and naphthalene results generally followed the distribution patterns apparent for total PAHs. Filtration was observed to decrease the total PAHs concentration slightly, with greater effects on the more hydrophobic PAHs, as expected. For total PAHs, total HPAHs, total cPAHs, and BaP, the unfiltered deeper (90 to 150 cm bml) Trident samples consistently showed higher concentrations than corresponding unfiltered shallow (0 to 38 cm bml) samples. Review of the fractional composition of the 17 individual chemicals that compose total PAHs shows a clear pattern of high naphthalene concentrations associated with high total PAHs concentrations offshore of the Gasco and Siltronic sites. For these high-concentration naphthalene locations, shallow (31 cm bml) Geoprobe samples generally had slightly higher concentrations than the collocated deeper (91 cm bml) samples. Additional evaluation of PAHs in TZW is provided in the detailed, site-specific discussions of groundwater pathways in Appendix C2.

D4.4.4 Patterns and Trends of TPH in TZW

TPH was sampled at six of the TZW sites (Kinder Morgan, ARCO, ExxonMobil, Gasco, Siltronic, and Willbridge Terminal). The highest concentrations of TPH in TZW were observed offshore of the Gasco and Siltronic sites, with the highest individual result measured offshore of the Gasco site. As shown on the histograms of the TPH map series, the distribution of unfiltered samples covers a larger and higher concentration range than the distribution of filtered samples; however, it should be noted that filtered TPH values do not include gasoline-range hydrocarbons (total petroleum hydrocarbons [gasoline]) (per sampling protocols for volatile organic compounds [VOCs], filtered samples of TPH [gasoline] were not collected). Focusing on diesel-range hydrocarbons—TPH (diesel)—and residual-range hydrocarbons—TPH (residual) (Table D4.1-1), it is clear, however, that filtration consistently decreases the concentration of these components. Further interpretation of this apparent effect of filtration is complicated by the expected variability in TPH composition (and corresponding hydrophobicity) from site to site (and likely sample to sample). TPH, as analyzed for the Round 2 investigation, is simply the measure of all hydrocarbons and non-hydrocarbons that can be quantified in the carbon range from $n\text{-C}_6$ to $n\text{-C}_{38}$, with no distinction/identification of specific component chemicals.

Comparison of TPH concentrations in the eight deep sample locations (90 to 150 cm bml) with the corresponding shallow results (0 to 38 cm bml) shows deep unfiltered results to be generally greater than shallow unfiltered results. Filtered deep results, however, show no clear trend. As discussed in Appendix C2, this information was evaluated in greater detail for each TZW study site in the consideration of groundwater pathway along with other lines of evidence.

To support consideration of patterns in the fractional composition of TPH, stacked bar charts are presented in Figures D4.4-3a–f, with one figure for each relevant TZW study site. Each figure presents results grouped by interpreted groundwater discharge zones. These zones are indicative of areas of similarly mapped groundwater discharge conditions offshore of the given study site and are discussed in detail in Appendix C2. These figures present both filtered and unfiltered results, with filtered sample IDs highlighted. As noted above, the filtered results for TPH do not contain TPH (gasoline) fractions. A general review of these figures reveals that, with few exceptions, duplicate results (indicated by “dup” in the sample ID) show similar composition and total concentration to the original sample.

Looking at the bar chart results site-by-site, there are few notable patterns in these plots relative to the interpreted zoning of groundwater discharge. Offshore of the Siltronic site, the “offshore discharge zone,” where there is a complete pathway for groundwater discharge of select VOCs (discussed in Appendix C2), shows a fairly clear TPH composition shift toward TPH (gasoline), as compared to the samples from the other Siltronic zones. (Note again that the highlighted filtered samples do not contain TPH [gasoline] in the TPH composition presented.) Similar increases in TPH (gasoline) fractional composition of TPH can be seen in samples offshore of the Gasco, ARCO,

and ExxonMobil sites; however, dominance of the TPH concentration in these unfiltered samples offshore of these sites is also generally accompanied by a sharp decrease in TPH concentration, making the pattern more difficult to interpret (possibly more reflective of the lack of TPH [diesel] and TPH [residual] than any increase in TPH [gasoline]). Further, these concentration ranges are close to detection limits, and the TPH (gasoline) results typically have lower detection limits (the average gasoline-range detection limit was 0.06 mg/L compared to 0.14 and 0.16 mg/L for TPH [residual] and TPH [diesel] samples).

In summary, the general nature of the analyte TPH (unknown mixture of anthropogenic and natural hydrocarbons and non-hydrocarbons that can be quantified in the carbon range from $n\text{-C}_6$ to $n\text{-C}_{38}$) significantly confounds detailed, source-related interpretation of results. Overall, filtration was observed to decrease the TPH (diesel) and TPH (residual) fractions. Review of the fractional components (diesel, residual, and gasoline) showed a composition shift toward TPH (gasoline) in the offshore discharge zone at the Siltronic site; however, patterns elsewhere were generally weak and more difficult to interpret when TPH concentration changes were also considered. Site-specific conclusions about groundwater pathways are presented in detail with additional lines of evidence in Appendix C2 and summarized in Section 4 of the RI report.